Theory of the optical properties of thin polycrystalline metal layers

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THEORY OF THE OPTICAL PROPERTIES OF THIN POLYCRYSTALLINE METAL LAYERS

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Résumé. — En faisant intervenir le caractère polycristallin de la structure des couches métalliques minces, on peut expliciter les composantes (réactive aussi bien que résistive) de l'impédance pelliculaire et les relier aux propriétés optiques. Dans les cas étudiés, la réactance a été identifiée à la capacité intergranulaire et reliée d'une manière simple à la structure géométrique du film. La liaison entre les propriétés optiques et la structure du film a été parachevée à l'aide d'une équation dans laquelle la résistance de l'espace frontière entre grains peut être calculée à partir des propriétés électroniques fondamentales de la substance.

Abstract. — By considering the polycrystalline structure of thin metal layers, reactive as well as resistive components of the sheet impedance can be identified and related to the optical properties. In the cases studied, the reactance has been identified with the inter-grain capacitance and has been related simply to the geometry of the film structure. A final link between the optical properties and the film structure has been achieved with the derivation of an equation by which the grain boundary resistance can be calculated from the basic electronic properties of the material.

Introduction. — It has long been recognized that the fine-grain structure of evaporated metal layers often results in anomalous optical properties. In 1952 the reactive contribution of the grain boundaries to the electrical impedance of polycrystalline films was established by optical measurements on evaporated bismuth [1]. It was shown that for wavelengths which are long compared with film thickness it is possible to account for the optical characteristics in terms of the complex impedance of the circuit network formed by the film structure. Capacitance between adjacent crystallites, or grains, was found to be the main source of reactance. In 1953 the idea of inter-grain capacitance was adopted also by Harris [2] to explain the optical properties of gold smoke deposits. The capacitance effect was discussed further by Mayer [3] in 1955. The results of a more detailed study of the problem were published in 1957 [5].

A typical polycrystalline structure is illustrated by the electron micrograph of evaporated bismuth shown in figure 1. The film structure is comprised of close-fitting polygonal crystallite grains separated by well defined plane grain boundaries. It has been established by overlap techniques that, for the most part, only single layers of crystallites are present. It was shown also that the average crystallite size is essentially equal to the average film thickness. The film structure with which we are concerned is illustrated schematically in figure 2.
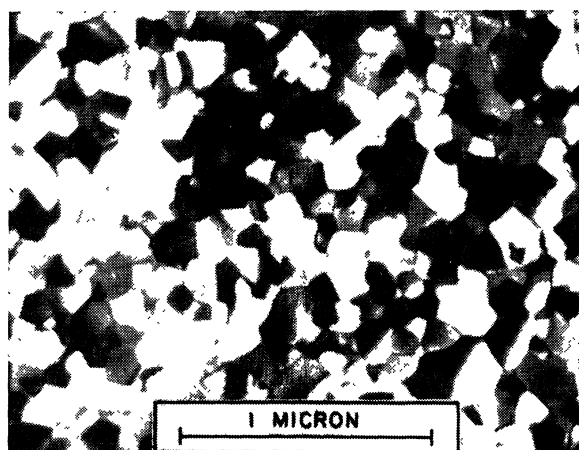

FIG. 1. — Electron micrograph of polycristalline bismuth film (75 ohms/square).

(a) TOP VIEW

CRYSTALLITE
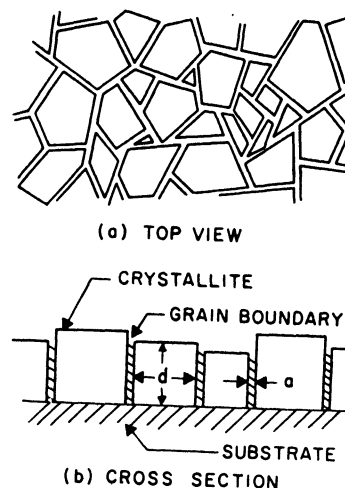GRAIN BOUNDARY
SUBSTRATE

(b) CROSS SECTION

FIG. 2. — Sketch of polycrystalline film structure. (a) Top view, (b) Cross section.

From a study of film resistance and its temperature dependence, and from low frequency electrical noise studies, it was established that the main contribution to the sheet resistance of evaporated bismuth films is the scattering of carriers at the grain boundaries [4, 5]. From infrared transmission studies it was concluded that the complete complex impedance of such films is derived from an actual random network of lumped-constant resistors and capacitors formed by the grain boundaries, the crystallites being the network conductors [1, 4, 5]. In addition it was concluded that a sharp division exists between those grain boundaries which conduct moderately well and those with essentially no conductivity [4]. The optical properties of such a film can be derived in terms of the unit network shown in figure 3, as illustrated by the curves for typical experimental
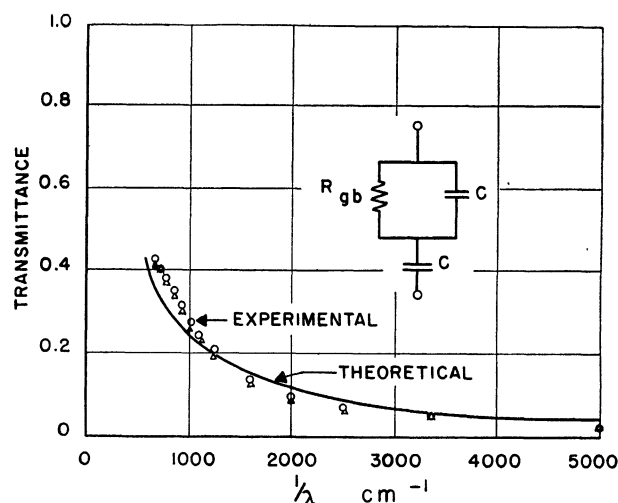

Fig. 3. — Infrared transmittance of polycrystalline bismuth films, experimental and theoretical (R_{dc} = 90 ohms/square, R_{gb} = 1/2 R_{dc}, C = 5.3 × 10⁻⁵ μμF).

and calculated infrared transmission characteristics. The slight discrepancy which is seen could be removed by assuming a small dispersion in the inter-grain dielectric material.

In the unit circuit the parameter C represents the mean value of inter-grain capacitance, and the resistance R represents the mean grain-to-grain resistance for those grain boundaries which contribute to the dc conduction. In the case of evaporated bismuth with a dc sheet resistance of around 100 ohms par square it was found that the grain boundaries were approximately equally divided between those which do and those which do not conduct [4, 5]. It follows, therefore, that R = 1/2 R_{dc}, where R_{dc} is the dc sheet resistance of the film in ohms per square [4].

For the evaluation of the circuit parameters the capacitance C is calculated from the infrared measurements, using either transmittance and

resistance or transmittance and reflectance data. From a knowledge of average grain size and the value C it is a simple matter to calculate the mean inter-grain spacing. Certain assumptions must be made about the effective dielectric constant, but calculations consistant with the electron micrograph observations suggest a mean inter-grain spacing of about 30 Å. In principle the value of C depends primarily on geometrical considerations with little relationship to the basic electronic properties of the film material.

The parameter R_{gb}, on the other hand, cannot be computed from geometry alone. It can be determined directly from a measurement of R_{dc}, or it can be deduced from transmittance and reflectance data. Such a determination of R_{gb} is adequate for a phenomenological calculation of theoretical optical properties ; however it does not provide a means of relating the optical characteristics to the basic electronic properties of the material.

The aim of the present work is to establish a theoretical relationship between the electronic properties and the sheet resistance. In the development of this theory the main task was the evaluation of electron scattering at the grain boundaries. A geometry was assumed for the film structure as shown in figure 2. In the calculation of electron penetration of grain boundaries a mechanism based on quantum mechanical tunneling was assumed. In the case of bismuth this theory has given not only the correct magnitude for film resistance, but it has also predicted the observed voltage and thickness dependences. In addition, the inclusion of diffusion conditions for film oxidation has, ior the first time, given a satisfactory explanation of an anomalous aging effect that had been observed on many films.

With the resultant equation for film resistance, as derived in this work, it is possible, finally, to calculate the optical properties of polycrystalline films from a knowledge of such quantities as the effective electron mass, electronic work function, Fermi energy, dielectric constant, and the film geometry.

Optical properties of polycrystalline films. — In order to accomodate all possible wavelength dependences of the optical properties of thin polycrystalline layers, it is necessary to describe the film behavior in terms of a number pair. Although it is customary to calculate the optical constants n and k, it is difficult to relate these numbers to physical features of the film structure in the case of close-fitting polygonal grains, as are being considered here. Since we are seeking a means of relating the interaction of electromagnetic waves with the structural features of a film, it seems more appropriate to consider the role of electrical impedance in describing the film characteristics. Thus,

it has been possible to describe, equally well, the optical properties with the number pair R and X, representing, respectively, the resistive and reactive components of the film impedance [4, 5]. Further, it has been found that the reactance X can be indentified with specific structural features of the film, as, for example, the inter-grain capacitance.

In terms of a general film impedance Z the optical properties for normal incidence are given by the equations [4].

$$\alpha = \frac{Z_0^2}{Z_0^2 + 2Z_0(Z + Z^*) + 4ZZ^*} \quad (1)$$

$$\beta = \frac{2Z_0(Z + Z^*)}{Z_0^2 + 2Z_0(Z + Z^*) + 4ZZ^*} \quad (2)$$

$$\gamma = \frac{4ZZ^*}{Z_0^2 + 2Z_0(Z + Z^*) + 4ZZ^*} \quad (3)$$

where α, β, γ are, respectively, the fraction of incident power reflected, absorbed, and transmitted. Z_0 is the characteristic impedance of free space (377 ohms/square). These expressions hold only for a film thickness which is small compared with the wavelength.

For the simple representation $Z = R + iX$, we can write.

$$\alpha = \frac{Z_0^2}{(Z_0 + 2R)^2 + 4X^2} \quad (4)$$

$$\beta = \frac{4Z_0 R}{(Z_0 + 2R)^2 + 4X^2} \quad (5)$$

$$\gamma = \frac{4(R^2 + X^2)}{(Z_0 + 2R)^2 + 4X^2} \quad (6)$$

In evaluating these equations both R and X must be related to a specific unit circuit. Thus, for the circuit configuration shown in figure 3, for example

$$R = \left[\frac{(\lambda/2\pi c)^2}{(\lambda/2\pi c)^2 + R_{gb}^2 C^2} \right] R_{gb} \quad (7)$$

and

$$X = \left[1 + \frac{R_{gb}^2 C^2}{(\lambda/2\pi c)^2 + R_{gb}^2 C^2} \right] (\lambda/2\pi c)^{1/C}. \quad (8)$$

Here R_{gb} is the mean grain boundary resistance in ohms for those grain boundaries which conduct, C is the mean grain-to-grain capacitance in farads, λ is the radiation wavelength in cm, and $c = 3 \times 10^{10}$ cm/s.

If the film geometry and the inter-grain dielectric constant K are known or assumed, the capacitance C can be calculated iimply from the parallel plate formula

$$C = (0.0884) Kd^2/a \quad \mu\mu F \quad (9)$$

where d is the average film thickness and a is the inter-grain spacing, both in cm, as shown in figure 2. In practice C is calculated from infrared transmission measurements [4], the grain size d is determined drom the electron micrographs, and a is calculated from equation (9). With the presence of oxide, impurities, and adsorbed gases in the grain boundary, the resultant dielectric constant K will certainly exceed unity. On the other hand an upper limit to the value of a can be ascertained from the electron micrographs, which in the case of bismuth films seems to be about 30 Å. From these results it is concluded that the effective value of K is of the order of 3.

Having established values for d, a and K, it is now possible to eliminate C and X by combining equations (8) and (9) with equations (4), (5) and (6). The resistance R (or R_{gb}) remains the only quantity in equations (4), (5) and (6) for which a theoretical evaluation has not been available. In the following section an equation is developed by which R_{gb} can now be calculated from the film geometry and the electronic properties of the material, thus providing a complete theory for the optical properties of polycrystalline thin films.

Electrical resistance of polycrystalline films. — The sheet resistance of very thin polycrystalline films is often found to be many orders higher than the highest possible values which could be expected from the most diffuse scattering of electrons at the film surfaces [5]. Such anomalous resistances can be understood only in terms of carrier scattering at the grain boundaries. Electrical noise studies of such films at very low frequencies have added further confirmation to the dominant role of grain-boundary scattering [5]. For definiteness the following discussion will be limited to the case of electron scattering.

In considering the details of a grain-boundary scattering mechanism, the idea of quantum mechanical tunneling has often been rejected because the usual strong, exponential dependences of current on voltage are not observed. A quantitative examination of the situation soon shows, however, how a tunnel mechanism for grain boundary penetration can actually predict an ohmic behavior.

If the potential drop resulting from a voltage applied across opposite edges of a film is considered to be divided only among the gaps formed by the grain boundaries, the field E within the intergrain space can be written, referring to figure 2, as

$$E = dV/al \quad (10)$$

where V is the applied voltage, and l is the length of the film between electrodes. In a typical case of a 100-ohm film V might be as high as 10 volts for $l = 1$ cm. If $d = 1\,000$ Å and $a = 30$ Å, the field E would be of the order of 300 volts/cm. Such a field can hardly be considered adequate to

induce field emission, which usually occurs only for fields in excess of 10^6 volts/cm.

The actual potential drop across each boundary space in the above example would not exceed 10^{-4} volt. When this value is compared with the normal range of work functions, which are at least the order of 1 eV, it is obvious that the applied field will have no significant effect on the intergrain potential barrier. Thus, if a tunnel mechanism is involved, the tunnel probability will be independent of the applied voltage.

From these considerations it is clear that the potential barrier can be represented schematically, at all normal voltages, as shown in figure 4. Since in this case the tunnel probabilities in the two directions are essentially equal, the net current flow can be shown to result from the unequal numbers of electrons available at the opposite grain interfaces, caused by the capacitor charging effect of the applied voltage. The excess charge might be less than one electron on each grain boundary ; however the number of coulombs per square cm is sufficiently high to account for the currents observed. In the case of bismuth, because of the anomalously low value for the effective electron mass, the tunnel probability might be as high as 0.1.

If we consider a square film with an edge dimension of l cm and a thickness d, as before, the total current I will be

$$I = jl \, d\eta \qquad (11)$$

where j is the current density in amp/cm^2 and η is the fraction of grain boundaries which conduct significantly well. Now j can be written

$$j = evP \, \Delta n \qquad (12)$$

where e is the electronic charge, v is the electron velocity, P is the tunnel probability, and Δn is the excess volume concentration of electrons on one side of the grain boundary in cm^{-3}. Further, we can write.

$$v = (2E_F/m^*)^{1/2} \qquad (13)$$

where E_F is the Fermi energy, and m^* is the effective electron mass.

Now, on each grain boundary the excess charge can be written as

$$Q = e(1/2d^2) \, \delta\Delta n. \qquad (14)$$

The grain boundary area is taken as $\dfrac{1}{2} d^2$ since the typical grain is assumed to be in the form of a right hexagonal prism with the height and major diagonal both equal to d. Here δ represents the effective depth or thickness of the excess charge layer in the crystallite, as indicated in figure 4.

Solving equation (14) for Δn and substituting with equation (13) into equation (12), we get

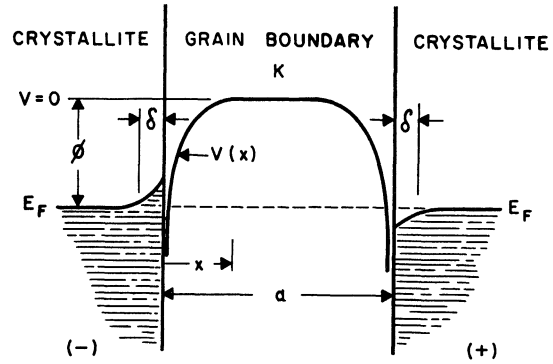$$j = (2Q/\delta d^2) \, (2E_F/m^*)^{1/2} \, P. \qquad (15)$$

FIG. 4. — Potential barrier in grain boundary.

In terms of the capacitance, $Q = aCE$. Or, from equation (10),

$$Q = CV(d/l). \qquad (16)$$

Combining equations (11), (15) and (16), we get

$$I = (2CV\eta/\delta) \, (2E_F/m^*)^{1/2} \, P. \qquad (17)$$

Since $R_{dc} = V/I$, we have

$$R_{cd} = (\delta/2C\eta) \, (m^*/2E_F)^{1/2} \, (1/P). \qquad (18)$$

Now, using $\dfrac{1}{2} d^2$ for the grain boundary area, as before, $C = 4.42 \times 10^{-14} \, (Kd^2/a)$ farad, where d and a are in cm. Substituting this expression into equation (18) gives

$$R_{cd} = \frac{8 \times 10^{12}(m^*)^{1/2} \, \delta a}{(E_F)^{1/2} \, Kd^2 \, \eta P} \text{ ohms/square.} \qquad (19)$$

Here m^* is in gm ; δ, a and d are in cm ; E_F is in ergs.

From a solution of the wave equation for a rectangular potential barrier [6] the approximate tunnel probability can be written, in terms of the notation in figure 4, as

$$P = [16 \, E_F \, \varphi/(\varphi + E_F)^2] \exp [-(2a/\hbar) \, (2m^*\varphi)^{1/2}] \qquad (20)$$

where the work function φ is also in ergs. Combining equations (19) and (20) we get, finally

$$R_{dc} = \frac{10^{12}(m^*)^{1/2} \, (\varphi + E_F)^2 \, \delta a}{2(E_F)^{3/2} \, \varphi Kd^2 \, \eta} \exp \left[\frac{2a}{\hbar} \sqrt{2m^* \, \varphi}\right]. \qquad (21)$$

In the general case $R_{gb} = \eta \, R_{dc}$, so that for the calculation of the optical properties from equations (4), (5) and (6) the values of R and X of equations (7) and (8) can be evaluated with the use of the following equation.

$$R_{gb} = \frac{10^{12}(m^*)^{1/2} \, (\varphi + E_F)^2 \delta a}{2(E_F)^{3/2} \, \varphi Kd^2} \exp \left[\frac{2a}{\hbar} \sqrt{2m^* \, \varphi}\right]. \qquad (22)$$

Results and conclusions. — In the case of evaporated bismuth the agreement in resistance values calculated from equation (21) with the observed values has been within 20 %, using the first choice

that was made for the most applicable values of the electronic parameters for bismuth and the mixed dielectric in the grain boundaries. From the best sources available, these were chosen as follows : $m^* = 10^{-2}\ m$, $\varphi = 1$ eV, $E_F = 0.23$ eV, $K = 3$, $\delta = 3 \times 10^{-7}$ cm, $a = 10^{-7}$ cm, $d = 10^{-5}$ cm, and $\eta = \dfrac{1}{2}$.

In addition to quantitative agreement with measured resistance values, several significant predictions from this theory have been substantiated by experiment. (1) Although the main conduction mechanism is by quantum mechanical tunneling across the grain boundaries, the theory predicts an ohmic behavior with respect to applied voltage. Constant resistance has been observed for applied voltages from 10^{-5} to 10 volts, a range of 10^6. (2) The theory predicts that the film resistance should be inversely proportional to the square of the film thickness. This dependence has been observed over a wide range of thicknesses as shown in figure 5. The quantitative agreement is
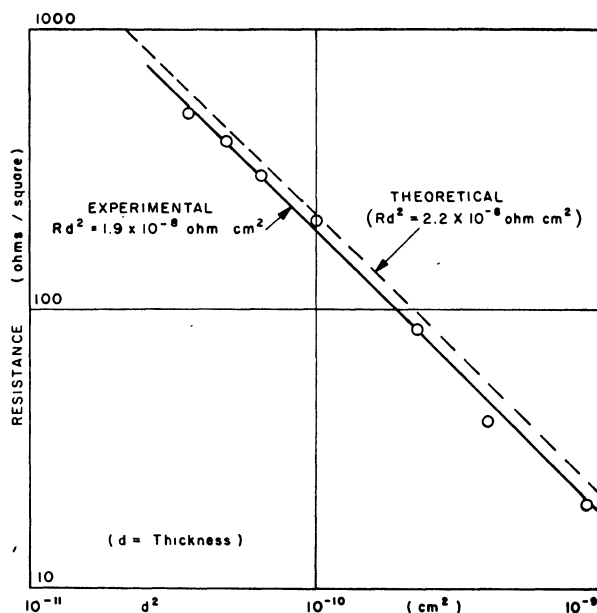

FIG. 5. — Thickness dependence of sheet resistance for polycrystalline bismuth films, experimental and theoretical.

also illustrated in the figure by a comparison of experimental and theoretical values of $R_{dc}d^2$. (3) With the inclusion of the diffusion conditions for the grain boundaries, an equation has been developed which explains for the first time the aging characteristics of evaporated bismuth films. The aging curves shown in figure 6 are typical of many more similar curves which have been measured on the rise in resistance due to oxidation.
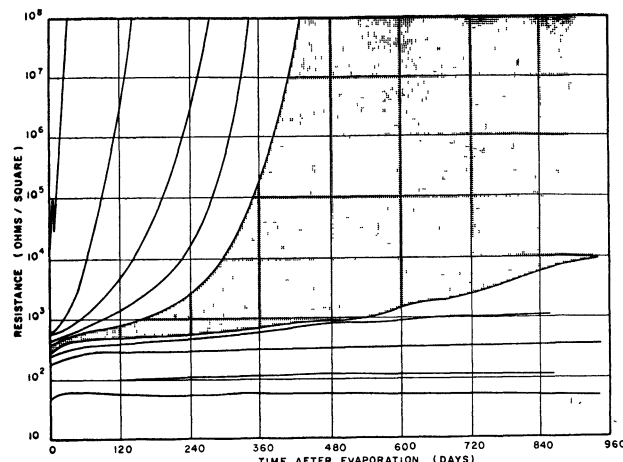

FIG. 6. — Drift of bismuth film resistance with age.

Never has te aging curve for any film been found to fall within the shaded area. The present theoretical aging equation shows this type of division in the long term stability of such films. Details of this latter work on film aging will be presented in a separate publication.

These results confirm the applicability, at least in the case of evaporated bismuth, of the resistance equations (21) and (22), and verify the tunnel mechanism for sheet conductivity. Calculations of film resistance based on this theory make it possible to predict, again with a high degree of success for evaporated bismuth, the optical properties from the basic electronic properties of the material and a knowledge of the film structure.

REFERENCES

[1] DRUMHELLER (C. E.), J. Optical Soc. Am., 1952, 42, 887.
[2] HARRIS (L.) and LOEB (A. L.), J. Optical Soc. Am., 1953, 43, 1114.
[3] MAYER (H.), Physik Dünner Schichten, Teil II, Wissenschaftliche Verlagsgesellschaft M. B. H., Stuttgart, 1955.
[4] DRUMHELLER (C. E.), Air Research and Development Command, Contract AF33(038)-21255 ; Report No.

21255-4, Sec. 3.2, 7 (April 1952) ; Report No. 21255-6 Sec. 3, 4 (October 1952) ; Report No. 21255-8, Sec. 3 (April 1953).
[5] DRUMHELLER (C. E.), Transactions of the Fourth National Symposium on Vacuum Technology, American Vacuum Soc., 1957, p. 27.
[6] MOTT (N. F.) and SNEDDON (I. N.), Wave Mechanics and its Applications, Oxford Press, 1948.